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# THE SOLIDIFICATION OF ALLOYS AND MAGMAS

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In this consideration of possible analogies in the solidification of alloys and igneous rocks, the treatment will be from a knowledge gained in the study of alloys, and with a confessed ignorance of the subject from the viewpoint of the geologist.

That the value of the views to be advanced is clearly recognized, and that their applicability extends beyond the limited sphere with which the writer is familiar, is well shown in the following extracts from the writings of Dr. George F. Becker,[1] of the United States Geological Survey. He says,

> In a plan submitted to the director when the new physical laboratory of the survey was first contemplated, I laid special stress upon the study of isomorphism and eutexia.

Also,

> It would appear that the relation between liquids must be reducible to very general groups. Liquids must be either miscible or immiscible, and miscible liquids must exhibit either isomorphic properties or eutectic ones.

And again,

> The applicability of eutexia to rock-classification depends upon the fact that it makes the systematic discussion of magmatic mixtures possible. Inasmuch as the subject-matter of lithology consists of mixtures, their classification must be carried out in terms of definite or standard mixtures, while the only mixtures possessing appropriate distinguishing properties are the eutectics. Thus in dealing with magmas or other heteromorphous miscible liquids, the eutectics seem to afford not only the best but the only natural and rational standards of reference. With any eutectic as a basis, a series of magmas may be prepared, each differing from the eutectic by containing an excess of one or more constituents.

Here, then, is the key to the whole discussion—the comparison of alloys and igneous rocks from the standpoint of isomorphism and eutexia, a standpoint which has its rational foundation on the laws of physical chemistry, more especially the theory of solutions and the phase rule of Gibbs. The application of these laws is of very recent date. In fact, it is hardly necessary to go back more than ten years to cover the period of their development. Because of this fact the drawing of well-worked-out analogies is very difficult; a considerable amount of investigation has been done with the simpler alloys, but in geology the field is practically barren. It will be necessary, therefore, to confine the discussion to the fundamental types of solidification from the viewpoint of their solubility relations, and to point out the application of these laws to certain alloys, and analogous minerals and rocks, wherever possible; leaving to the judgment and imagination of the reader the possibility of their further application to geological problems.

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[1] Day and Allen, *Isomorphism of the Feldspars* (Publications of the Carnegie Institution). Introduction by Dr. George F. Becker.

Proceeding from this viewpoint, it is at first essential to grasp a few fundamental facts. Alloys are solutions, and obey the same laws in freezing as aqueous solutions of salts do in crystallizing. It is merely a question of fluidity at a different range of temperature. Not only is this true, but it is likewise true that solubility is not limited to any particular state of the interacting substances. Thus we may have solubility in the solid state, or solid solutions. This is shown in the tendency for mutual diffusion of solid gold and solid platinum; or more well known, perhaps, in the harveyizing of armor plate, where carbon is absorbed by iron at temperatures well below the point of fusion. These solid solutions you are more familiar with as isomorphous mixtures or mixed crystals.

## COOLING-CURVES

In obtaining the solubility curves for salts in solution, the usual procedure is to make analyses of the saturated solution at various temperatures, and in this way to obtain a series of points which may be plotted into a temperature-composition curve. In the case of alloys, this method is not so well suited, since we are working at higher temperatures; also we often have to deal with changes in the solid, as well as in the liquid state. For alloys we obtain the necessary data for individual mixtures by means of the cooling-curve, a curve which is a function of time and temperature, and shows the change in the rate of cooling as the temperature is lowered. Breaks in the curve or changes in direction indicate an evolution or absorption of heat, and denote a change of state or a transition in the substance. In practice, the general method is to heat a metal or alloy of known composition to a desired temperature, introduce a pyrometer, and record the temperature at stated time-intervals during cooling.

Such curves are shown in Fig. 1. The one on the left represents the cooling of pure platinum. Temperatures are plotted on the vertical axis, and time on the horizontal. Starting at o, our metal cools gradually, until we reach 1,775°. Here we have a jog in the curve, an arrest in the temperature change due to the freezing of the metal and the evolution of the heat of solidification. Freezing completed, the material cools to room temperature without further break in the curve.

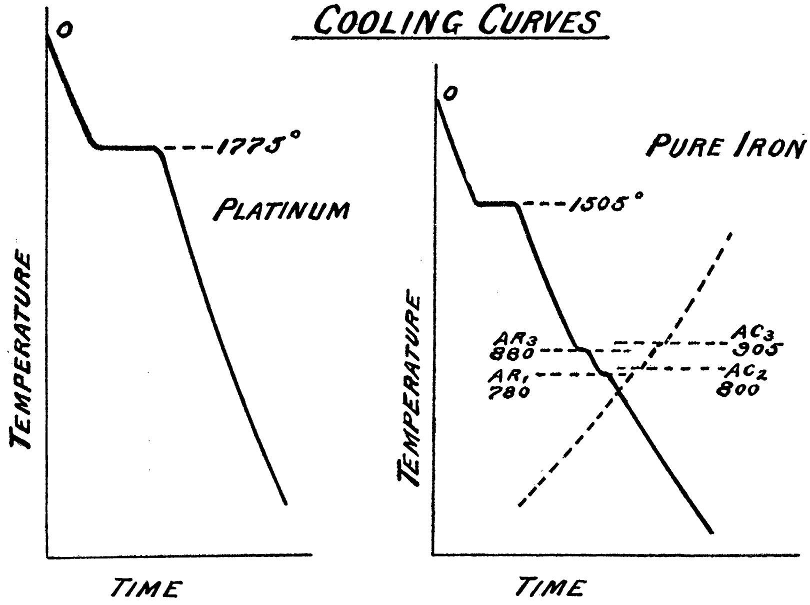

FIG. 1

On the right we have another cooling-curve, that of pure iron. Starting again at o, the metal cools to 1,505° when there is a break due to the solidification. On further cooling, we note a different condition from that observed in the case of platinum. There are two other jogs in the curve, at 880° and 780°, denoting changes in the solid state. These represent the transition points of the three allotropic modifications of pure iron, and are designated as the $\alpha$, $\beta$, and $\gamma$ states. These allotropic states represent changes in the properties of the iron without change of composition, and are analogous to some cases of pleomorphism in minerals; for example:

$$\text{Sulphur}\left\{\begin{matrix}\text{orthorhombic}\\ \text{to}\\ \text{monoclinic}\end{matrix}\right\}96^\circ \qquad \text{Leucite}\left\{\begin{matrix}\text{pseudo-isometric}\\ \text{to}\\ \text{isometric}\end{matrix}\right\}500^\circ$$

FREEZING-POINT CURVES

In the investigation of alloys, we consider three general types of solubility relations; with complete miscibility in the molten state it may after solidification be complete, partial, or nil.

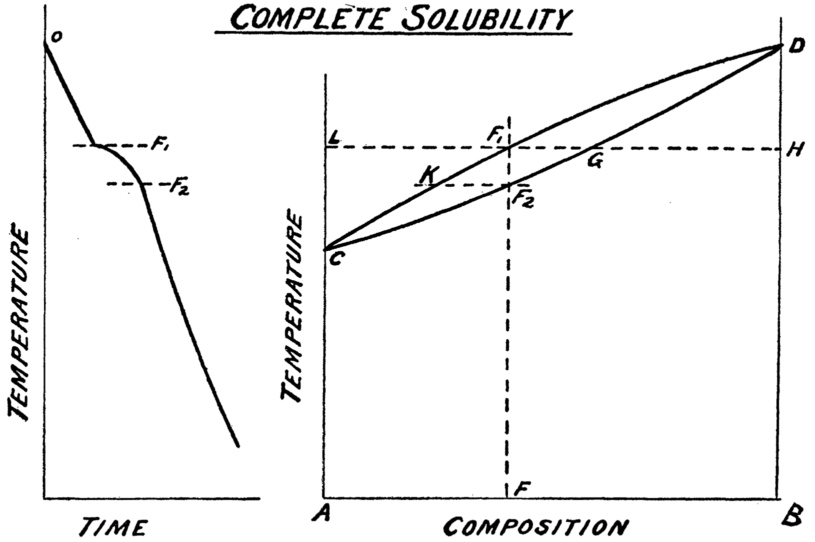

FIG. 2

Referring to Fig. 2, we have represented the type of complete solubility before and after solidification. On the left is the cooling-curve for a single mixture. We note two breaks, at $F_1$ that due to commencement of solidification, and at $F_2$ a change of direction due to its completion. With points for commencement and completion of solidification obtained from similar cooling-curves representing a complete series of mixtures, we may plot a new diagram with the composition on the *X* axis, and the corresponding freezing temperatures on the *Y* axis, and obtain the solubility curve as shown on the right of Fig. 2. In metallography this is usually designated the "freezing-point curve." $CF_1D$ and $CF_2D$ are the loci of the upper and lower transition points as obtained from the cooling-curves, and represent, therefore, the commencement and completion of solidification for the entire range of mixtures.

With this type of freezing, a mixture of composition *F*, for example, will commence to solidify at $F_1$ with a separating-out of the first frozen particle of composition *G*, a consequent relative enrichment of the molten metal in element *A*, and a lowering of the temperature of solidification. During freezing, therefore, the temperature-composition locus of the molten material will shift along the upper curve from $F_1$ toward *C*, and that of the solid material along the lower curve from $G_1$ toward *C*. If cooling is sufficiently slow because of the complete solubility in the solid, the equilibrium is completed by the diffusion of the different solid particles until finally the resultant alloy has a uniform composition $F_2$ the same as the original molten mixture.

With complete solubility, therefore, the freezing is selective but not rigid, and the initial heterogeneousness is effaced by diffusion. Under the microscope, the structure should be uniform throughout if diffusion is complete.

Of this type are the Sb-Bi, Ag-Au, Fe-Mn alloys.

The type of complete insolubility is shown in Fig. 3. On the left is the cooling-curve, with a break at $K_1$, indicating commencement of solidification, and a jog $K_2K_2$ denoting completion of freezing at a constant temperature. At the right is the freezing-point diagram, with $FE_1G$ and $CE_1D$ as the loci of commencement and completion of solidification. A mixture of composition *K* will commence to freeze at $K_1$. The solid separating out will be element *A* only, because of the complete insolubility; there will be a relative enrichment of the molten solution in *B*, and a gradual shifting of the temperature composition range from $K_1$ to $E_1$. At $E_1$ the whole of the remaining solution will freeze at this constant temperature; but because there is no solubility in the solid *A* and *B* will separate.

For a mixture of composition *E*, freezing will occur throughout the mass simultaneously, with a separation in the solid state of *A* and *B*. In like manner, for alloy *M*, freezing will be as explained above, except that element *B* will first separate out, with a gradual enrichment of mother metal in *A*, and a gradual lowering of the freezing temperature, until at $E_1$ there will again occur the isothermal solidification of the remaining solution, with separation of *A* and *B*.

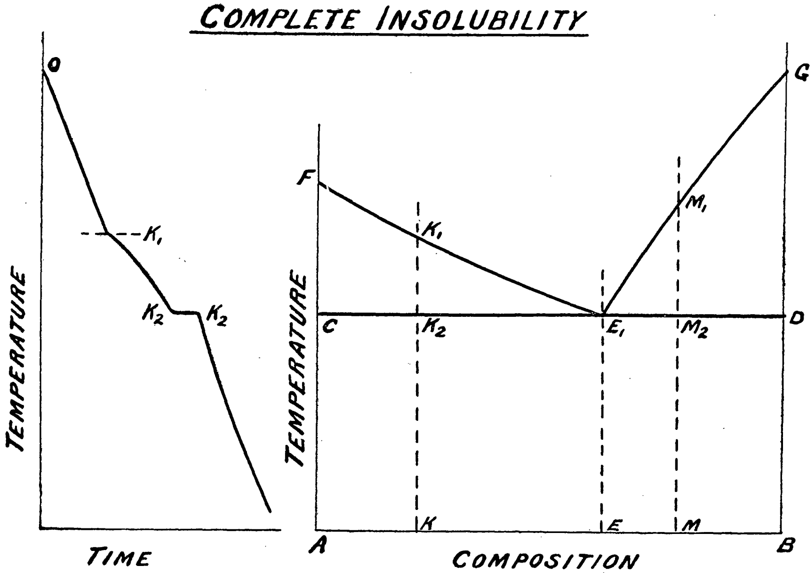

FIG. 3

The point of lowest freezing temperature $E_1$ is called the eutectic point, and the mixture of this composition, the eutectic mixture, or the eutectic.

Summarizing, we have in this type rigidly selective freezing, with alloys eutectiferous throughout the range of composition, and no tendency for mutual diffusion. Under the microscope we should expect to find a more or less segregated excess metal *A* or *B*, depending upon whether the initial composition was above or below the eutectic ratio; together with an intimate composite structure of *A* and *B* as the eutectic.

Of this type are the Sb-Pb, Pb-Sn, Cd-Zn alloys.

A third type of freezing-point curve is that of partial-solubility solid, as shown in Fig. 4. This condition is really a combination of the two types previously described. For mixtures between *JF* and *GK*, freezing will be of the type of complete solubility. Between *F* and *G*, the freezing will be selective, as in the complete insolubility type, except that, since there is partial-solubility solid, the excess metal to separate out will be saturated with the other element; and the eutectic will be a composite of *A* saturated with *JF* per cent. of *B* and *B* saturated with *GK* per cent. of *A*.

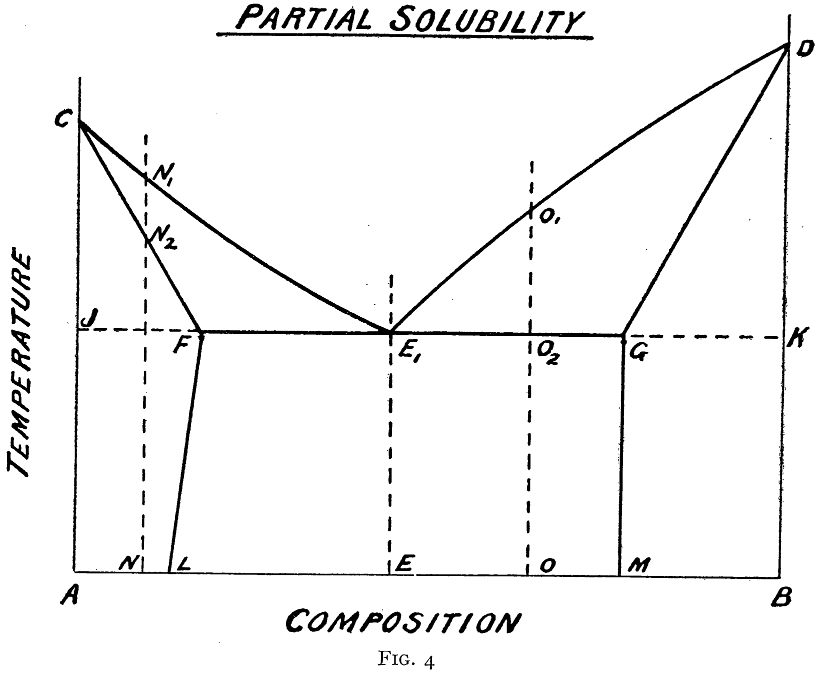

FIG. 4

With this type of freezing, therefore, we have freezing with complete solubility at the two ends of the series, and under the microscope we should find a homogeneous structure. For the intermediate mixtures there will be selective freezing and under the microscope we should expect a heterogeneous structure of an excess substance either *A* saturated with *B* or *B* saturated with *A*, depending upon whether the composition of the original molten mixture lay to the left or right of the eutectic ratio; and a composite eutectic $A$ saturated with $B$ and $B$ saturated with $A$.

Of this type are the Sn-Zn, Au-Ni, Ag-Cu alloys.

Besides these three general types of solubility which we have considered, numerous others could be taken up in detail. For example, $A$ and $B$ might form one or more definite compounds, which compounds could have with $A$ and $B$ and with each other, independently different solubility relations. Or again, there might be only partial solubility while the alloy was still molten. However, all are really combinations and elaborations of the fundamental types to fit more complicated conditions.

## ISOMORPHISM OF FELDSPARS

Referring now to one of the few investigations in this line which have been carried out in geological research, we have (Fig. 5) the freezing-point curve of the soda-lime feldspars, as determined by Day and Allen[1] at the Geophysical Laboratory of the Carnegie Institution. The work was conducted exactly as indicated for alloys, by time-

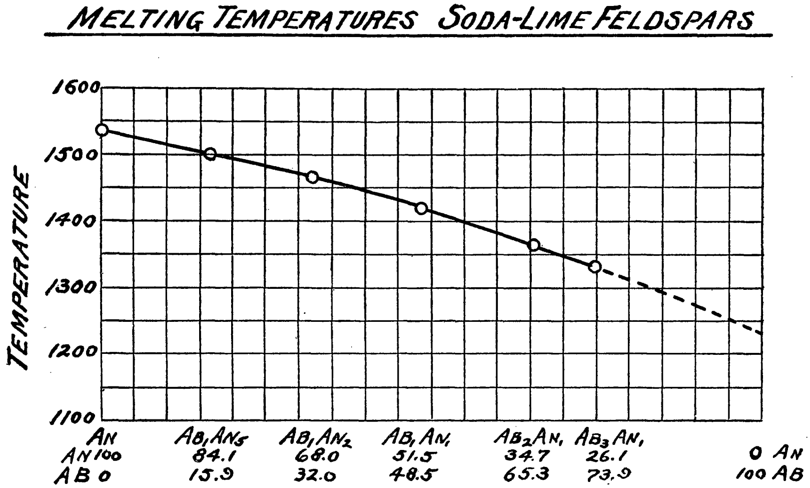

FIG. 5

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[1] Day and Allen, *Isomorphism of the Feldspars* (Publications of the Carnegie Institution).

temperature records of the desired mixtures. Because of the undesirable supercooling, Day and Allen, however, recorded the heating, rather than the cooling, curve. As will be seen from the diagram, it is of the complete solubility type, with no indication of eutectics or intermediate compounds. It is conclusive evidence that between 100 per cent. of anorthite and 100 per cent. of albite we have an isomorphous series; and microscopic examination was entirely confirmatory.

### IRON-SILICON ALLOYS

Fig. 6 shows the freezing-point curve of the iron-silicon alloy,[1] chosen because it represents a rather complex set of conditions. At

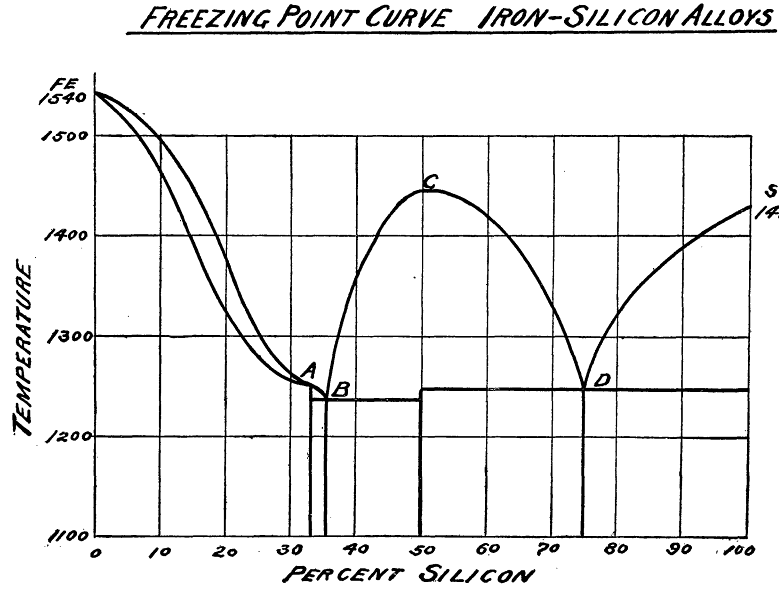

FIG. 6

*A* there is evidence of the formation of a compound, the silicide $Fe_2Si$. At *C* (50 atoms per cent. Si) another compound is indicated, of the composition FeSi. Up to $33\frac{1}{2}$ atoms per cent. of Si, the curve is of the type of complete solubility, with resulting solid solutions of iron and $Fe_2Si$. Between $33\frac{1}{2}$ and 50 per cent., $Fe_2Si$ and FeSi are immiscible, and we have completely eutectiferous freezing. This is also the case between 50 per cent. and 100 per cent. Si, with the two components FeSi and Si.

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[1] W. Guertler and G. Tammann, "Ueber die Verbindungen des Siliciums mit dem Eisen," *Zeitsch. f. anorg. Chemie*, 1905.

### CALCIUM AND MAGNESIUM METASILICATES

Strictly analogous to this is the diagram (Fig. 7) of solidification of calcium and magnesium metasilicates, also determined at the Geophysical Laboratory of the Carnegie Institution by E. T. Allen and W. P. White.[1] As will be seen, at 47 per cent. $MgSiO_3 + 53$ per cent. $SiO_3$ there is indication of the formation of the compound $MgSiO_3$ $CaSiO_3$ the mineral diopside. This diopside breaks the diagram into two parts each of the partial-solubility type. For the left-hand side,

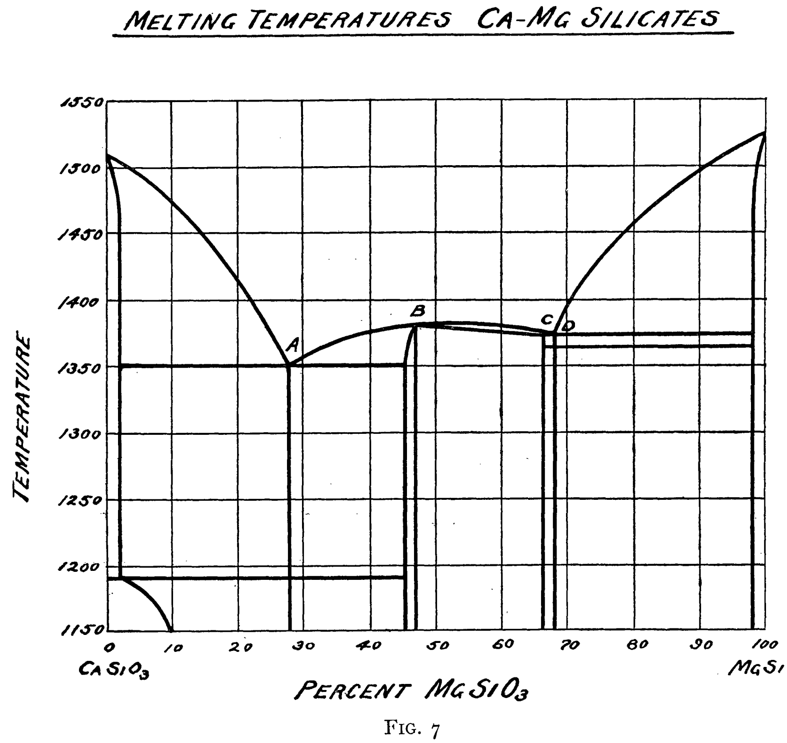

FIG. 7

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[1] Allen and White, "Diopside in Its Relations to Calcium and Magnesium Metasilicates," *Am. Jour. Sci.*, January, 1909.

solid solutions of $CaSiO_3$ and diopside will separate out between 0 and 2 per cent. and 46 and 47 per cent. of $MgSiO_3$. From 2 per cent. to 46 per cent., the structure will be a composite eutectic of $CaSiO_3 +$ diopside, each saturated with a small amount of the other, and an excess substance of $CaSiO_3$ or diopside, each saturated with the other, depending upon whether the composition is below or above the eutectic composition of 28 per cent. $MgSiO_3$.

Likewise for the right-hand half of the diagram, isomorphous mixtures of diopside and $MgSiO_3$ are indicated between 47 and 67 per cent. and 98 and 100 per cent. of $MgSiO_3$. Between 67 and 96 per cent. a eutectic will form of $MgSiO_3$ and diopside each saturated with the other, and an excess substance diopside below the eutectic composition of 68 per cent. of $MgSiO_3$, and $MgSiO_3$ above this ratio. This diagram also furnishes an example of a condition frequently met with in alloys, that of allotropy, or transitions below the solidification range. Thus above 1,190° the $\alpha$ $CaSiO_3$, or pseudo-wollastonite, is the stable form, but is unknown in nature; below this temperature the $\beta$ form, the mineral wollastonite, is stable. With $MgSiO_3$ the $\beta$ form is magnesian pyroxene occurring in meteorites and intergrowths with enstatite. At 1,365° this is transformed into the orthorhombic $\alpha$ form distinct from enstatite and unknown in nature.

Microscopic examination confirmed these deductions except that the eutectic texture was rarely met with, probably due to the very slow cooling and consequent segregation of the constituents.

## EUTECTICS AMONG ROCKS

Work of this general nature, but not so reliable and accurate, has been done by J. H. L. Vogt on the silicates, and he mentions a number of eutectic mixtures, as follows:

| | | |
|---|---|---|
| 68 per cent. diopside | with | 32 per cent. olivine |
| 74 per cent. melilite | “ | 26 per cent. olivine |
| 65 per cent. melilite | “ | 35 per cent. anorthite |
| 40 per cent. diopside | “ | 60 per cent. akermanite |
| 74.25 per cent. anorthite | “ | 25.75 per cent. quartz |
| 75 per cent. albite | “ | 25 per cent. quartz |

## THREE COMPONENT MIXTURES

So far the discussion has been confined to the freezing of two component mixtures. However, more generally, particularly in rock magmas, three or more constituents will be present. This greater number of components will admit of the possibility of greater multiplication of the solid phases forming and results in a very much more complicated problem. Unfortunately, there have been published the results of but very few investigations along this line, and these only for very simple cases. To represent the equilibrium of a three-component mixture we make use of the property of an equilateral triangle that if from any point within perpendiculars be dropped upon each of the three sides, the sum of the lengths of these perpendiculars is a constant, and equal to the altitude of the triangle. Consequently with an equilateral triangle as a base, each apex of which represents respectively 100 per cent. of *A*, *B*, and *C* constituents, and temperatures plotted perpendicular to this base, we obtain a space-model, with the equilibrium between the solid and liquid phases, or, in other words, the locus of the solidification points of each particular mixture, represented by a set of warped surfaces, very much as topography is represented on a relief map. And just as we represent the elevations of this relief map on a plane surface by means of contour lines of equal elevations, so do we represent the temperatures of our space-model of solidification, by contour lines of equal temperatures, or, as technically called, by isotherms.

Such a representation is shown in Fig. 8, for the solidification of the Bi, Pb, Sn alloys.[1] These have the simplest relations for a three-component alloy, since no intermediate compounds are formed, and there is complete insolubility between the constituents. The dotted lines are the isotherms for the commencement of solidification. The altitudes at each angle denote 100 per cent. of each of the elements Pb, Bi, and Sn. The triangle is divided into three regions by the lines *GE*, *IE*, and *HE*, which correspond to our previous freezing-point loci representing the primary separation of one of the three pure components. Consider an alloy of composition *A*. The point denoting this alloy lies in the region Bi, *GEI* on the isotherm 175°. At this temperature, therefore, pure bismuth commences to separate out. The alloy becomes successively poorer in bismuth as the temperature is lowered, and, since the ratio of tin to lead must remain constant, the composition shifts along the line *AC* from *A* to *C*. At 125° we meet the line *IE*. At this temperature, therefore, a binary eutectic mixture of bismuth and tin now separates out and the composition of the mixture is displaced along the line *IE* until finally at point *E* corresponding to a temperature of 96°, the ternary eutectic

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[1] G. Charpy, "Study of the White Alloys Called Antifriction," *Metallographist*, Vol. II, 1899.

FREEZING POINT DIAGRAM

LEAD-BISMUTH-TIN ALLOYS

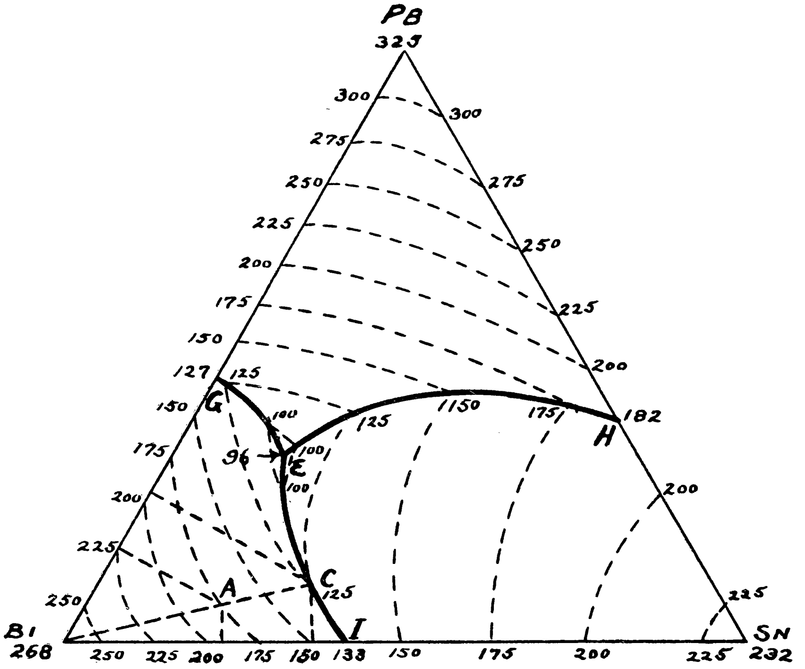

FIG. 8

51½ per cent. Bi, 15½ per cent. Sn, and 33 per cent. Pb freezes at constant temperature.

This is about the limit of our capabilities in indicating the solidification conditions. For a greater number of components, or where other factors enter, the representation becomes a space-problem of four or more dimensions, which is really beyond our powers.

## COMPARATIVE MICROGRAPHS

Figures 9, 10, and 11 show the striking similarity between the structure of rocks and alloys as revealed by the microscope. In each case the rock-section is on the right, beside its analogous alloy-structure on the left.

In the upper left-hand corner of Fig. 9 is the structure of a three-component mixture of 74 per cent. Bi, 5½ per cent. Sn, and 21 per cent. Pb. The excess bismuth has separated out into the white masses; surrounding these is the binary eutectic of bismuth and tin, and finally, as the central black constituent, we note the ternary eutectic. A somewhat similar rock-texture is on the right, a rhyolite with the white quartz, the dark orthoclase, and the finer remaining ground mass.

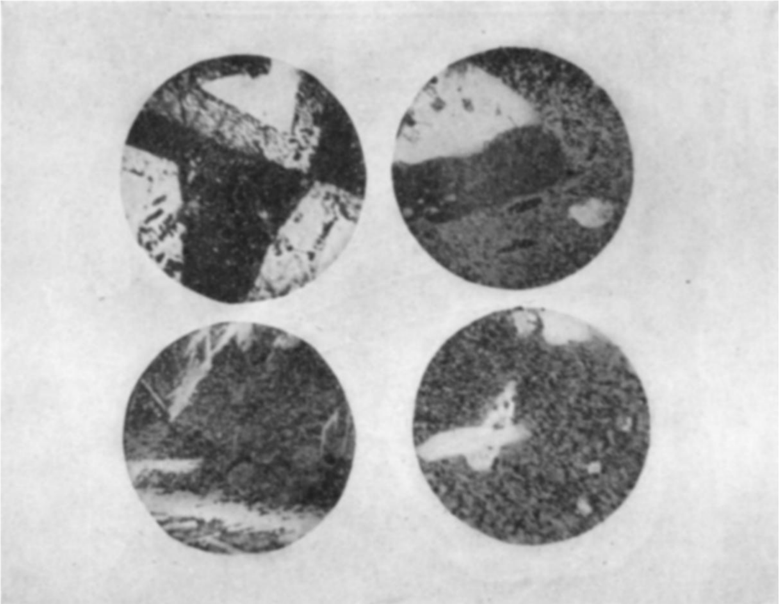

FIG. 9

Below on the right is a section of Augite porphyry, with the white plagioclase, adjoining this the gray augite, and inclosing all the fine texture of the ground mass of plagioclase and augite. It is very similar to the metal structure on the left, a steel with an excess cementite, and a eutectic pearlite, made up of this cementite and ferrite.

It is not the purpose of this article to discuss these sections in detail by trying to point out their methods of freezing; it is desired solely to show that two such classes of material as metals and rocks, widely different as they are ordinarily considered to be, in reality display the same peculiarities of texture.

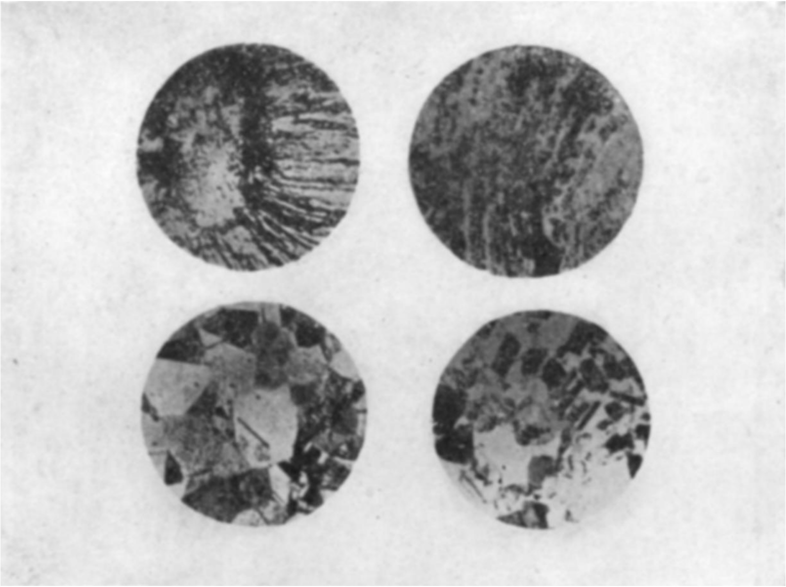

FIG. 10

## APPLICATIONS TO IGNEOUS ROCKS

In endeavoring to point out the similarities in the solidification of certain alloys and magmas, one is limited to simple cases to which the theory of solubilities is easily applied. That the same considerations apply to the igneous rocks is indisputable; for it is not a question of drawing an analogy between the alloys and rock-masses. It is, rather, the application of broad general principles to specific problems; the application of general laws of equilibrium which must cover all possible cases of solution, even though as yet we may be unable to apply the details of their working. The igneous rocks are, as a rule, very complex, and may contain many component minerals or elements; also there is an additional complication in that solidification takes place very often under pressure. Pressure is of great importance in the consideration of vapors, and so difference of pressure may introduce additional complexity through the effect on the gases. Again, equilibrium conditions may not always be reached; for example, with rapid cooling of the magma, supersaturation may have occurred with a change in the order of deposition of the minerals, or differences in the microscopic structure.

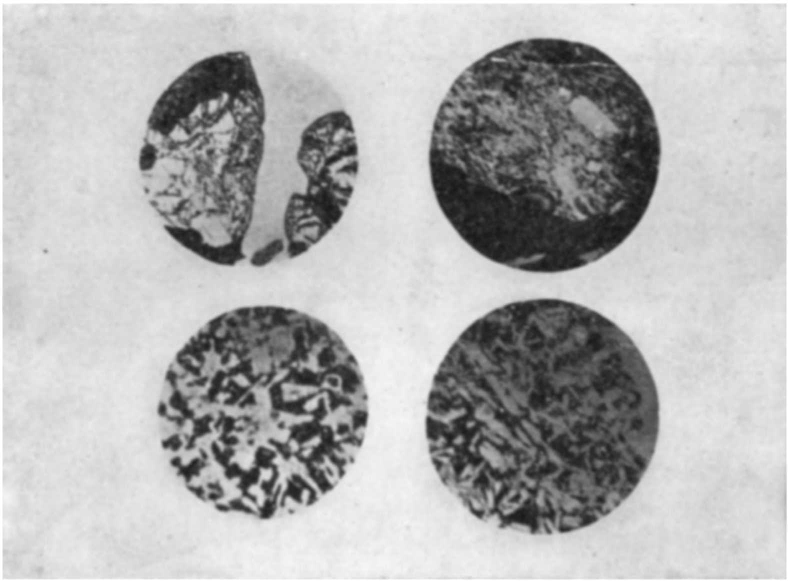

FIG. 11

In the solidification of magmas, also, we have certain conditions which do not occur in the metallic alloys. We have discussed the composite nature of the eutectic structure. Among the metals, where the cooling is normal, this intimate mixture of the constituents is very common; with the slow cooling of the igneous rocks (especially when enhanced by their poor conductivity of heat) the long sojourn just below the temperature of transition may cause a segregation of the eutectic constituents, and an elimination of the composite texture.

Furthermore, we do not make alloys in which the components are not perfectly miscible when molten, because in this case there will be separation by liquation and a defeat of the object sought by the mixture of the metals. But igneous-rock mixtures are not of man's choosing. Consequently there will very likely often be encountered the case of mixtures of imperfect miscibility, with a first separation of the components of saturation, and their final solidification according to the laws of freezing.

To clear up the intricacies of the problem, it is essential that extended research be conducted along the line of the few cases already worked out, beginning with the simpler conditions and extending the scope as circumstances warrant. With the electric furnace, desired minerals or rocks could be melted and could also be synthesized under any pressure; the pyrometer would give us the thermal reactions; finally with the microscope we could compare the structure of our artificial material with the natural rock in its original and remelted states. An investigation of this kind may reduce cases of seeming complexity to ones of comparative simplicity, by fixing a certain few of the components as of primary importance, and the rest of a secondary modifying nature. For example, while steel is a many-component alloy of Fe, C, Si, S, P, and Mn, we treat it as a two-constituent mixture of Fe and C as of greatest importance; the other elements have their influence mainly in their effect on the transition ranges of the carbon and iron.

At any rate, the thermal investigation has the great advantage of getting at the internal reactions, and can be backed up by our present methods with the microscope, and otherwise, which are suitable only for the end reactions.

In conclusion, it is well to bear in mind that the laws of equilibrium of solutions show that the melting-points of the constituents are of no service in predicting the order of their separation in the solidification of the magma. And is it going too far to predict that the study of the freezing-point diagrams of the conditions of this separation may result, as did Van't Hoff's application to the carnallite deposits at Strassburg, in economies in the recovery of the metals from their ores?